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**A Relaxation Study of Poled Nonlinear Optical Polymers by Infrared
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A RELAXATION STUDY OF POLED NONLINEAR OPTICAL POLYMERS BY INFRARED REFLECTION-ABSORPTION SPECTROSCOPY

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Abstract - The relaxation of poled nonlinear optical (NLO) chromophores in polymer films was characterized by infrared reflection-absorption spectroscopy. Both a guest-host system and a photocrosslinkable polymer system were investigated. Polymethylmethacrylate doped with either 2-methyl-4-nitroaniline or 4(4'-nitrophenylazo)aniline was studied. The photocrosslinkable polymer system, polyvinylcinnamate doped with 3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenyl azo]nitrobenzene was also investigated. Doped NLO active molecules were aligned using the corona poling technique. Infrared spectra as a function of time were used to monitor the relaxation behavior of the oriented dyes after poling. Relaxation of NLO molecules was followed at various characteristic vibrational frequencies. The relaxation behavior of both systems were found to be consistent with those studied by the second harmonic generation technique.

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INTRODUCTION

Amorphous polymers doped with organic chromophores with large second-order hyperpolarizabilities have become promising materials for nonlinear optical (NLO) applications. These materials are attractive because of their large nonlinear susceptibility and relative ease of processing. They have been proposed for use in many applications such as electro-optic switching and modulation, second harmonic generation (SHG), and optical signal processing [1-3].

Second order nonlinear optical properties can be obtained by the alignment of doped organic chromophores in a polymer in a noncentrosymmetric manner. Several classes of second order NLO polymers have been studied, such as Langmuir-Blodgett films [1,4], guest-host systems [5-7], and materials containing NLO moieties covalently linked to either the side chains [8,9] or the polymer main chains [10,11]. Thermal [12,13] or photochemically [14-16] crosslinked systems, and materials incorporating NLO chromophores in quasi-organic matrices [17,18] have also been investigated. Alignment of dipoles is usually achieved by applying a large electric field across the polymer film, namely poling. The electric field can be obtained by either corona discharge [5,7,9,19] or applying an electric potential between two electrodes [7,13,20]. Poling is usually carried out at a temperature near the glass transition (T_g) of amorphous polymers where the increased mobility of polymer chains eases the movement of chromophores. The orientation of chromophores is retained by cooling down the temperature well below T_g in the presence of the field. Since poled ordered NLO chromophores in the polymers provide the second order NLO properties, it is important to

study the orientation of these chromophores and the temporal stability of the poled order.

The degree of orientation of chromophores in poled polymers and their relaxation is often studied by the SHG technique [5-7,20-23]. By monitoring SHG as a function of time, the relaxation of oriented NLO dyes in a polymer can be observed. The second harmonic coefficient which is proportional to the square root of the second harmonic (SH) intensity, is related to the angle between the poling field and the average molecular axes of the poled dye molecules [6,24]. The angle changes as the dipoles start to relax and lose their orientation. This leads to a decrease in the SH intensity. In addition to the SHG method, UV-visible spectroscopy [6] and waveguiding experiments [19] have also been used as tools to study the orientation distribution of chromophores and the optical anisotropy of poled polymer films. The decay of the field-induced anisotropy shows a relaxation of the aligned dipolar molecules.

Infrared spectroscopy has been used as a tool for studying the orientation of polymers using infrared dichroism [4,25-28]. However, using IR spectroscopy to study the relaxation of aligned NLO chromophores as a function of time has not been reported in the literature. It is easy to carry out an IR measurement as compared to SHG or waveguide experiments. Unlike the results from other techniques which only monitor the relaxation of the poled order, IR spectra also provide information about the vibrational energies of various functional groups within the material. This allows us to monitor chemical or physical changes of not only the chromophores but the polymer system as a whole. These advantages over other techniques motivated us to use IR

spectroscopy as a characterization tool for the study of the relaxation of NLO molecules.

In order to demonstrate the use of IR spectroscopy for the study of the relaxation of the poled order, well established polymer systems (viz. a guest-host system and a photocrosslinkable polymer system) are chosen for this study. In this paper, the investigation of the dynamics of the rotation of dopants dispersed in amorphous polymers was performed by means of polarized infrared reflection-absorption spectroscopy.

EXPERIMENTAL PROCEDURES

1 g of polymethylmethacrylate (PMMA) and 0.2 g of 2-methyl-4-nitroaniline (MNA) were dissolved in 10ml of 1,4-Dioxane and was filtered through filter membranes (pore size 0.2 μm). The solution was spin-coated onto a glass slide coated with 1500 Å Aluminum. The sample was soft baked at 50 °C for 12 hr. PMMA doped with 4(4'-nitrophenylazo) aniline (Disperse Orange 3, DO3) samples were prepared in the same manner. MNA and DO3 obtained from Aldrich Chemical Co. were recrystallized once prior to use. Figure 1 shows the chemical structures of MNA and DO3.

1 g of polyvinylcinnamate (PVCN, Polysciences, Inc.) and 0.3 g of 3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenyl azo] nitrobenzene (CNNB-R) were dissolved in 15 ml of 1,4 Dioxane. The synthesis of CNNB-R has been reported previously [29]. The solution was first filtered and then spin-coated onto a glass slide coated with 1500 Å of aluminum. Subsequently, the sample was baked at 80 °C for 18 hr.

The sample is poled by applying a high electric potential (~3k volts) across a sharp tungsten needle and the grounded heating stage which supports the sample. The heating stage provides thermal control during the poling process. The corona discharge results in the accumulation of surface charges on the top of the polymer film. These charges produce a static field across the film which is responsible for the alignment of the dipoles. The aluminum layer was grounded during the poling process. Poling of the PMMA doped with MNA or DO3 were performed at 70 °C for 15 min. The samples were quenched to room temperature in the presence of the corona field. Samples show no phase separation before and after the poling process. IR measurements were performed as a function of time at room temperature for 20 hr.

PVCN doped with CNNB-R samples were poled at 70 °C for 15 min. The sample was quenched to room temperature and then exposed to UV radiation for 20 min with the poling field left on. A multi-ray UV lamp (Gates, Inc.) was used for photocrosslinking. An intensity of 2 mw/cm² at 254 nm was chosen. The IR spectrum was recorded immediately after the poling process. The sample was then placed in an oven with a preset temperature of 70 °C. After a certain period of time, the sample was taken out and quenched to room temperature before an additional IR measurement was taken. The sample was again placed back into the oven after the measurement. This heating and cooling cycle was repeated throughout the relaxation study of the photocrosslinking system.

FTIR spectra were collected with a Perkin-Elmer 1760 FTIR spectrometer at 4 cm⁻¹ resolution as a function of time. A Perkin-Elmer variable angle specular reflectance accessory was used to obtain the

reflection-absorption spectra. An incident angle of sixty degrees was chosen for this study. A wire grid polarizer was used to obtain the desired polarization. For time dependent reflection-absorption spectroscopy, an incident polarization parallel to the plane of the sample was chosen. Figure 2 shows the experimental setup for obtaining reflection-absorption spectra and the sample geometry for the measurement.

RESULTS AND DISCUSSION

Figure 3 shows changes in the IR reflectance spectra as a result of poling and relaxation of MNA in PMMA. The IR measurement was performed after poling, at 60° incident angle with a polarization parallel to the polymer film. After the sample was poled, the molecular dipoles of the MNA molecules tend to be aligned along the direction of the electric field. Therefore, these dipoles are preferentially oriented vertical to the substrate which reduces the overlap between the IR radiation E field and the transition dipole moment. This leads to a decrease in absorbance, or in other words an increase in the measured reflectance. As the relaxation of dipoles starts, the reflectance decreases continuously. Sublimation of MNA was observed at elevated temperatures and must have occurred to some extent during the poling process. This physical loss of the chromophore also contributes to the increase of measured reflectance. An undoped PMMA film was also poled for comparison. The carbonyl peak at 1735 cm^{-1} showed an increase in reflectance after poling. Besides, it was found that the baseline of the spectrum was slightly shifted. For our analysis of the NLO molecules, we have found that the magnitude of the reflectance changes due to the poling of the host polymer is negligible. Reflectance

changes due to relaxation of dipoles were also observed in other functional groups. The results are summarized in Table 1. Figure 4 shows several vibrational modes for a triatomic functional group. The atomic vibrations shown here are all in the same plane.

The transition dipole moments of the nitro group for both symmetrical (ν_s) and asymmetrical stretching (ν_{as}) vibrations are perpendicular to each other.⁴ When the NLO dyes are oriented, the transition dipole of ν_s tends to move away from the plane of the sample. Therefore, during the dipolar relaxation a decrease of reflectance due to the increased absorbance is observed as shown in Figure 5(a). Since the molecules are not perfectly oriented, the plane normal of the nitro group does not have a specific direction associated with the substrate normal. In addition, the transition dipole of ν_{as} does not have a preferred direction with respect to the polarization of the incident IR radiation. We did not observe a significant intensity change for ν_{as} of DO3 compared to the case of ν_s as shown in Figure 5(b). Moreover, it was found that the ν_{as} peak shifted from 1522 cm^{-1} to 1520 cm^{-1} after poling. The peak shifted back towards the original value during the relaxation process. Similar results were obtained in the case of MNA. In addition, the reflectance of ν_{as} increased during the relaxation process which is opposite to the case of ν_s . The observed changes are smaller than the reflectance changes of ν_s . The reason for the field-induced peak shift is not clear at this stage. However, the different relaxation behaviors between ν_s and ν_{as} of the nitro group may suggest a method for assisting the peak assignment in the IR spectra.

Figure 6 shows normalized reflectances vs. time after poling at wavenumbers corresponding to NH_2 scissoring of both MNA (1640 cm^{-1})

and DO3 (1632 cm^{-1}) molecules. The reflectance of the samples right after poling was assigned to be unity. The reflectances measured at different time periods were normalized accordingly. MNA shows a faster relaxation rate at the initial stage than DO3. In addition, MNA shows a larger percentage of decrease in reflectance over a period of 20 hr. This result is similar to that obtained from the SHG measurement [5]. The relaxation processes of NLO chromophores in an amorphous polymer matrix are strongly affected by the glass transition temperature of the polymer, the molecular interactions in the system, and the size of the chromophores. The reason that the relaxation of MNA is faster than DO3 is due mainly to the size difference of the molecules since DO3 and MNA have similar functional groups (Figure 1) but are different in their molecular sizes. The spatial rotation of the chromophore during relaxation is affected by the distribution of the local free volume around the dye molecules in these polymers. Therefore, MNA rotates more easily than DO3 in the PMMA matrix which leads to a more rapid decrease in reflectance for MNA than DO3.

For the photocrosslinkable system, relaxation of poled NLO dyes were found to be extremely slow at room temperature due primary to the large molecular size of CNNB-R. Therefore, the relaxation of the photocrosslinking system was performed at $70\text{ }^{\circ}\text{C}$. Figure 7 shows the FTIR spectra of PVCN doped with 30% CNNB-R, before and after poling without UV treatment. A polarization perpendicular to the incident plane was chosen for monitoring the relaxation behavior. The spectra show a significant reflectance increase after poling since the dipoles tend to orient in the direction normal to the polymer film. During the annealing process

at 70 °C, the sample showed a rapid change of reflectance at the initial stage of annealing followed by a further gradual decrease toward the original intensity before poling.

In comparison, Figure 8 shows the FTIR spectra of poled PVCN doped with 30% CNNB-R with subsequent 20 min of UV irradiation. A rapid relaxation was also observed after annealing at 70 °C for 5 min. However, after this initial change the reflectance at 1609 cm^{-1} remained fairly constant during further annealing. Our studies have shown that during UV irradiation, a certain degree of degradation took place which resulted in a decrease of absorbance and hence a corresponding increase of reflectance. UV induced degradation complicated the interpretation of the experimental results. Therefore, SHG measurements were used to support our analysis. A weak SHG signal was observed for both UV treated and untreated samples after 3 hr of annealing at 70 °C. However, after an additional 24 hr of heat treatment at 70 °C, SHG signal of the sample treated with UV radiation was still quite evident. In contrast, the sample without UV irradiation showed no SHG signal at all. The result confirmed that the stability of the photocrosslinked sample was improved through the UV crosslinking reaction.

CONCLUSIONS

Reflection-absorption IR spectroscopy was demonstrated to be a technique useful for the study of the relaxation of poled NLO molecules. Relaxation can be monitored at various vibrational frequencies. Field-induced peak shifts were found for the asymmetrical stretching vibration of

the nitro groups. The relaxation behavior of the poled order is similar to that obtained from the SHG measurement for all samples studied.

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(Legend to the Table)

Table 1. Relaxation observed at the various frequencies and the corresponding molecular vibrations for the functional groups of MNA.

cm ⁻¹	Assignments	Reflectance changes during the relaxation
3464	$\nu_{as}(\text{NH}_2)$	increases
3383	$\nu_s(\text{NH}_2)$	decreases
1640	$\delta_s(\text{NH}_2)$	decreases
1608, 1588	Aromatic ν (C-C)	decreases
1486	$\nu_{as}(\text{NO}_2)$	increases ^a
1313	$\nu_s(\text{NO}_2)$	decreases

^a A peak shifted to higher wavenumbers was observed.

(Legend to the Figures)

Figure 1. Chemical structures of (a) MNA and (b) DO3.

Figure 2. Experimental setup for reflection-absorption infrared measurements. Polymers were spin-coated onto a glass slide coated with 1500Å aluminum. A wire grid polarizer was used.

Figure 3. IR spectra of MNA in PMMA. Curves shown from top to bottom are: right after poling, 120 minutes after poling, and pristine.

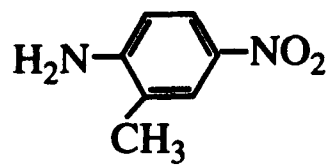
Figure 4. Molecular vibrational modes for (a) scissoring (δ_s) of NH_2 (b) symmetrical stretching (ν_s) of NO_2 (c) asymmetrical stretching (ν_{as}) of NO_2 .

Figure 5. IR spectra show the relaxation of the nitro group for DO3 in PMMA as a function of time. (a) symmetrical stretching. Curves shown from top to bottom are: right after poling, 40, 120, 570 minutes after poling, and pristine. (b) asymmetrical stretching. Curves shown from right to left are: right after poling, 570 minutes after poling, and pristine.

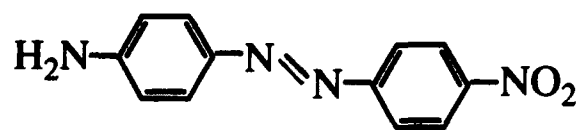
Figure 6. Reflectance changes at wavenumbers which correspond to NH_2 scissoring as a function of time after poling for PMMA doped with MNA and DO3.

Figure 7. Relaxation of poled PVCN doped with 30% CNNB-R at 70 °C. Curves shown from top to bottom are: right after poling, 5,10,20,80 minutes of annealing, pristine.

Figure 8. Relaxation of poled and UV irradiated PVCN doped with 30% CNNB-R at 70 °C. Top and bottem curves are right after poling and pristine samples respectively. Overlaped curves which are shown in the middle are for 5,10,20,80 minutes of annealing after poling.

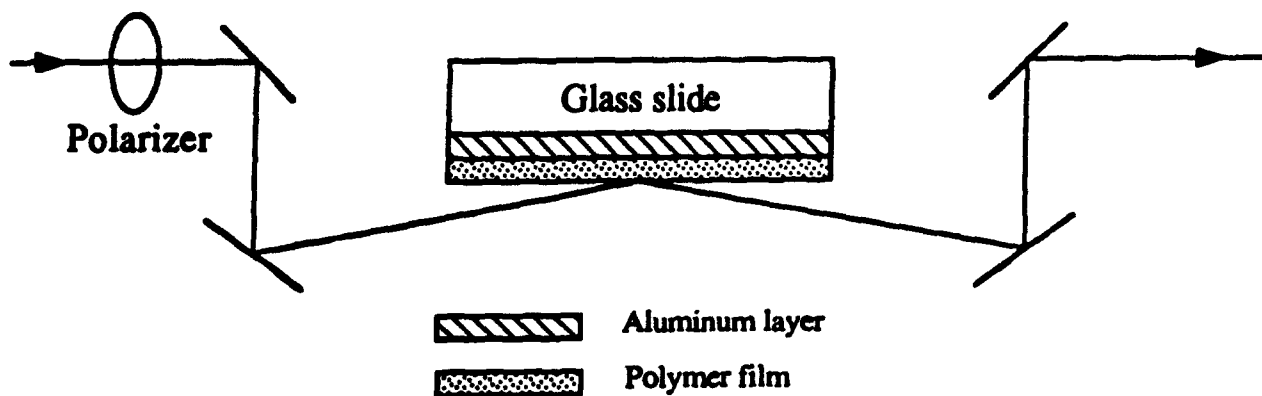


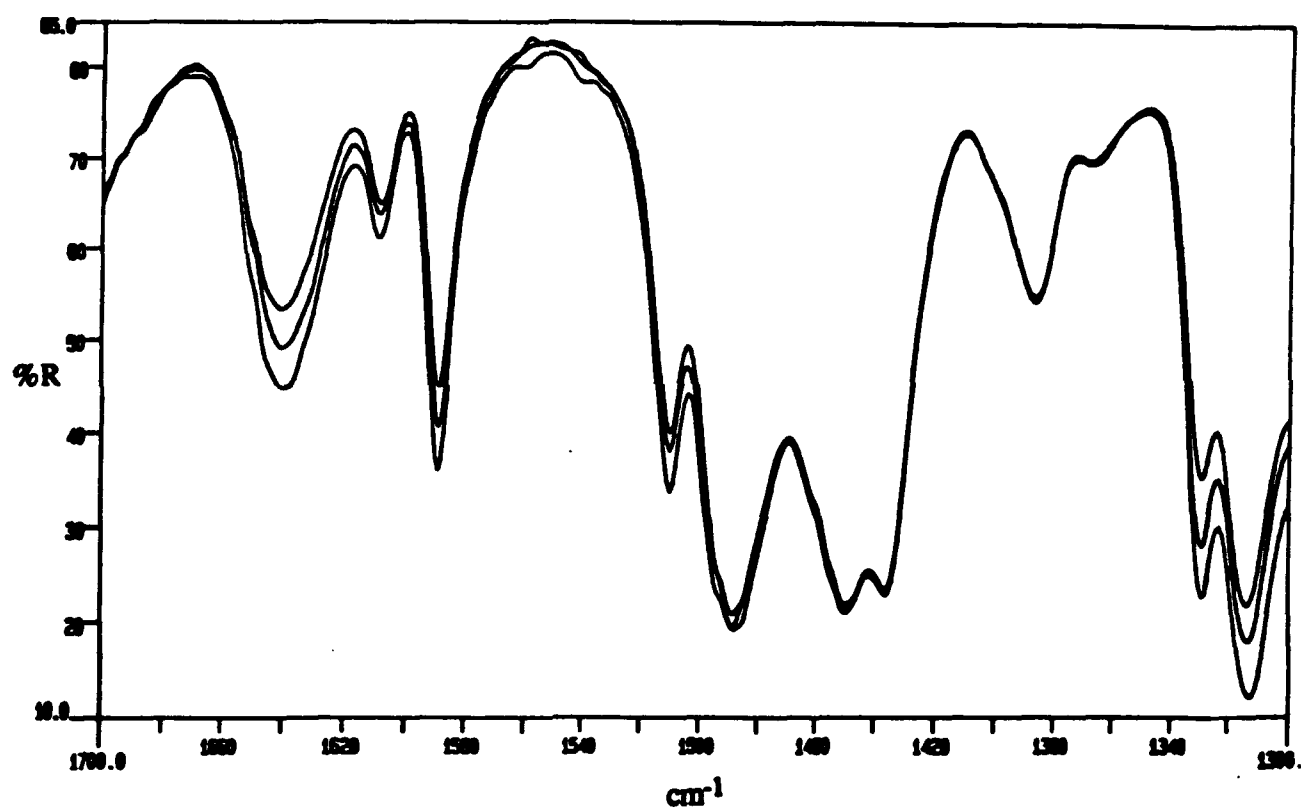
(a)

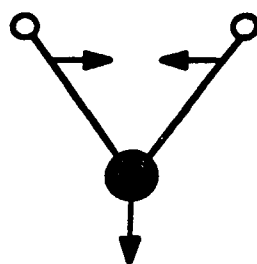


(b)

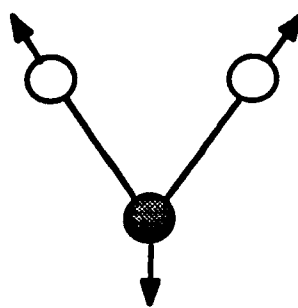
Incident IR radiation



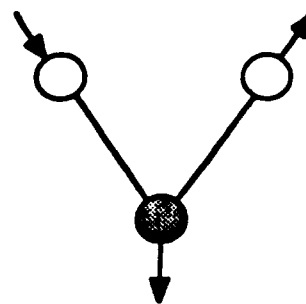




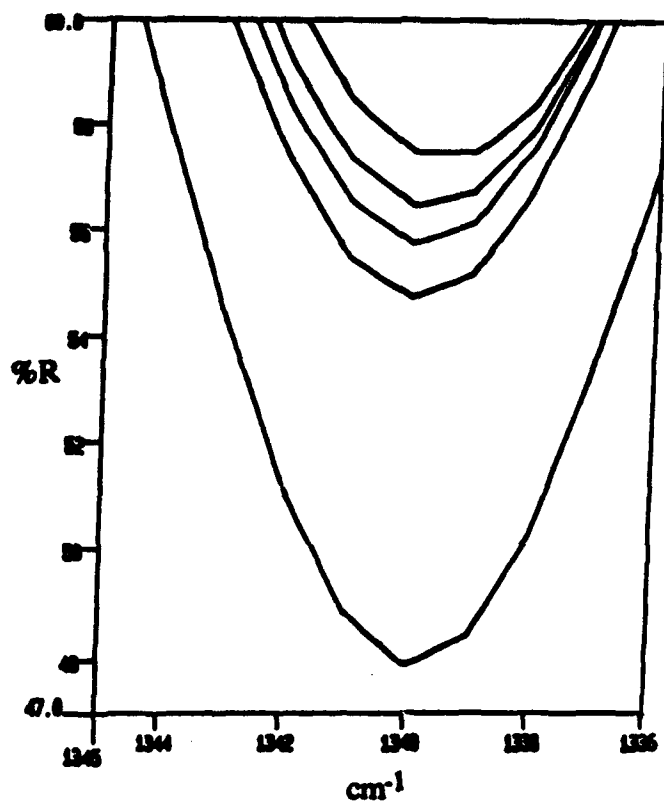
(a)



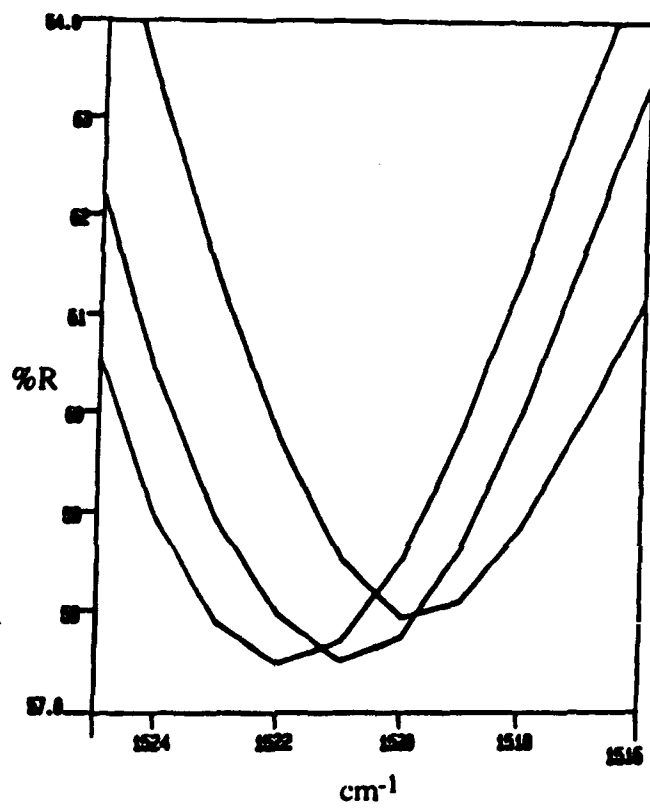
(b)



(c)



(a)



(b)

